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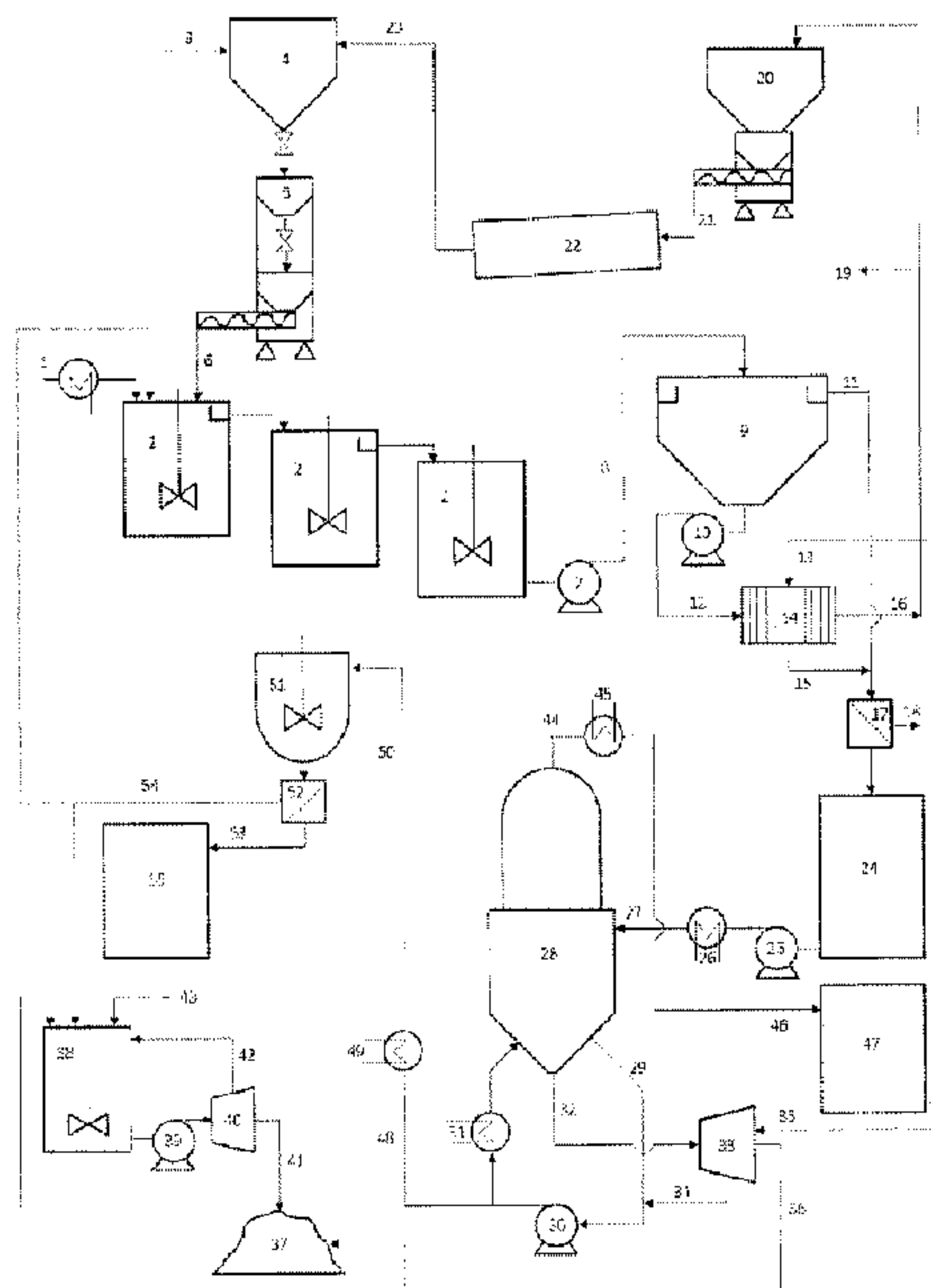
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(54) Titre : PROCEDE DE FABRICATION DE PRODUITS D'HYDROXYDE DE SODIUM ET DE CHLORURE DE SODIUM A PARTIR DE SAUMURE USEE

(54) Title: PROCESS FOR MANUFACTURE OF SODIUM HYDROXIDE AND SODIUM CHLORIDE PRODUCTS FROM WASTE BRINE



(57) **Abrégé/Abstract:**

The present invention provides a process for the manufacture of sodium hydroxide and sodium chloride products from a waste brine stream containing sodium chloride, and at least sodium carbonate or sodium bicarbonate. The method of this invention comprises converting the sodium carbonate and/or sodium bicarbonate to sodium hydroxide through addition of lime to the brine, while simultaneously converting impurities to less soluble forms to facilitate their removal. The causticized brine is separated from unreacted lime, calcium carbonate and solid impurities to produce clean brine with reduced levels of impurities. The brine is then concentrated by evaporation, forming relatively pure sodium chloride crystals, which are extracted and rinsed to reduce alkali contaminants. The process continues until sodium hydroxide solution strength of about 46-50 % is reached, with cooling of the solution and separation of crystallised salts further reducing impurities to a comparable level to diaphragm cell derived industrial grade sodium hydroxide.

ABSTRACT

The present invention provides a process for the manufacture of sodium hydroxide and sodium chloride products from a waste brine stream containing sodium chloride, and at least sodium carbonate or sodium bicarbonate. The method of this invention comprises converting the sodium carbonate and/or sodium bicarbonate to sodium hydroxide through addition of lime to the brine, while simultaneously converting impurities to less soluble forms to facilitate their removal. The causticized brine is separated from unreacted lime, calcium carbonate and solid impurities to produce clean brine with reduced levels of impurities. The brine is then concentrated by evaporation, forming relatively pure sodium chloride crystals, which are extracted and rinsed to reduce alkali contaminants. The process continues until sodium hydroxide solution strength of about 46-50 % is reached, with cooling of the solution and separation of crystallised salts further reducing impurities to a comparable level to diaphragm cell derived industrial grade sodium hydroxide.

PROCESS FOR MANUFACTURE OF SODIUM HYDROXIDE AND SODIUM CHLORIDE PRODUCTS FROM WASTE BRINE

FIELD

The present invention provides a process for manufacture of industrial grade sodium hydroxide and sodium chloride products from a waste brine stream containing sodium chloride, and at least sodium carbonate or sodium bicarbonate. The invention is particularly applicable in providing a beneficial use for waste brine generated during treatment of waters co-produced during coal seam gas extraction, but may be applied to any sodium chloride rich brine stream with a substantial sodium carbonate and/or sodium bicarbonate component.

RELATED PATENT APPLICATION

[0001] This application claims priority to Australian Provisional Patent Application Number 2013902526, filed 9 July 2013, which is herein incorporated by reference in its entirety.

BACKGROUND

[0002] Brackish and saline waste waters are generated from a variety of processes including extraction of oil and gas, minerals processing, power generation and manufacturing industries. In the coal seam gas (CSG) industry large volumes of water are co-produced with gas from the wells, and generally the water quality is such that treatment is required prior to use or disposal. Treatment processes, for example reverse osmosis, usually produce clean water by separating and concentrating the dissolved salts into a brine stream. The brine, typically containing 1-6 % total dissolved solids, poses a significant disposal problem, which existing disposal and beneficial use options have not satisfactorily resolved.

[0003] Brine from the CSG industry, as generated for example in Queensland Australia, has a high concentration of sodium chloride and substantial levels of sodium bicarbonate and sodium carbonate. For example, the sodium chloride may comprise about 40-90 % of the dissolved solids, and the sodium carbonate and sodium bicarbonate about 10-60 % of dissolved solids, with other contaminants such magnesium, calcium, silica and potassium typically less than 2 % of the dissolved solids.

[0004] Given the high concentration of sodium chloride and sodium carbonate/bicarbonate, the ideal solution would cost effectively separate and process these components into marketable products. Unfortunately existing processes developed to treat and dispose of mixed brine streams of this type, or to recover salts for beneficial use, have significant limitations. These include sub-optimal environmental outcomes due to incomplete recovery of salts and/or water and hence a residual waste problem, adverse economics due to high capital and operating costs, and limited value-add or quality risk in terms of the products.

[0005] One of the brine disposal methods used within the oil and gas industry is injection into a geological formation, such as a deep aquifer already containing salty water, which is isolated from other aquifers which are of beneficial use to the community and which are not connected in any way with shallow groundwater and surface water systems. Within the CSG industry, injection into depleted CSG wells has also been proposed. Brine disposal by this method is thus dependent on availability of suitable geological formations and/or depleted wells. There is substantial risk and cost associated with establishing re-injection wells, and risks around the compatibility of the brines with the formation fluids which may impact permeability around the well bore and lead to plugging. Furthermore, increasing regulatory requirements and community concern related to potential environmental impacts and long term sustainability of brine injection, are contributing to its cost and complexity. Primarily due to the lack of readily identifiable suitable deep aquifers, and lack of depleted wells when required, some of the major CSG projects in Queensland have concluded that brine injection is not a viable option, and all are investigating other alternatives.

[0006] Another method used for disposal of brines is evaporation to a dried mixed salt, either utilising conventional solar ponds, assisted solar methods, or mechanical evaporation and crystallisation/salt drying. An example of such a process is described in U.S. Patent No. 5,695,643 assigned to Aquatech Services, which in one of the embodiments concentrates the brine then utilises a dryer to produce a low moisture content mixed salt. Regardless of the evaporation and crystallisation/drying method, these processes result in a mixed salt with no commercial value which must be disposed of as a waste. Since the salts are highly soluble and harmful if released to the environment, they need to be stored in a regulated waste facility. The construction and ongoing monitoring of these facilities is expensive, and is not proven to provide an acceptable permanent disposal solution for soluble salts.

[0007] In order to recover salt for beneficial use, a low-tech process has been proposed for brines comprised primarily of sodium chloride, which involves dosing hydrochloric acid into the brine to convert the sodium carbonate and sodium bicarbonate into sodium chloride. Evaporation and crystallisation of the treated brine, containing about 98% sodium chloride, results in a crude salt which could be washed to a saleable product. Alternately, utilising established brine purification methods from the chlor-alkali industry, the brine can be concentrated to saturation in an evaporator and then treated prior to crystallisation to remove magnesium and calcium as insoluble salts. This results in production of a higher purity sodium chloride product. While this process is beneficial in avoiding the substantial costs associated with managing a mixed salt, it utilises relatively costly acid to produce lower value sodium chloride. Hydrochloric acid demand for brines from the CSG industry are high at about 1.5-2.1 tonne of 33% acid per tonne of contained sodium carbonate and bicarbonate. This could equate to an acid cost of around \$ 630 per tonne of sodium carbonate/bicarbonate in brine, which taking into account the low value of sodium chloride negates any prospect of product value exceeding the input costs.

[0008] More sophisticated processes involving the selective precipitation of salts have been proposed in recent patent applications, such as that by HPD described in Patent Pub. No. US 2012/0213689 A1. The application proposes a process comprised of several concentration and evaporation/crystallisation stages, to produce sodium carbonate and sodium chloride products. A patent application has been lodged by HPD in Australia for the same process under Appl. No. AU 2011201691. The HPD application describes production of sodium carbonate via a multi-stage process, whereby it is first extracted in decahydrate crystal form, which is further processed into dense soda ash or sodium bicarbonate for sale via recrystallisation. A similar recrystallisation process is envisaged for beneficiating extracted sodium chloride. The process generates a concentrated liquid waste stream which will require disposal or further processing. Further processing could for example involve evaporation to a dry mixed salt requiring disposal. While the process produces marketable products, it is relatively complex and will be costly due to the number of unit operations and refining steps involved. The process fails to address the fate of unconverted sodium bicarbonate remaining in the brine stream after concentration, which typically could be about 1.5% by mass. Furthermore, the process produces a concentrated waste stream, albeit of much reduced volume, which requires further processing or disposal.

[0009] An alternative selective salt recovery process is described in Australian Patent Application No. AU 2011202102 A1 by Penrice Soda Products. In fact the essential elements of this process are not novel and have already been commercialised for manufacture of soda ash from naturally occurring brine in two large scale operations, namely at Searles Lake in the US, and Sua Pan in Botswana. The process involves carbonation of the brine to convert about 85-90% of the sodium carbonate to sodium bicarbonate. Upon cooling the brine the relatively insoluble sodium bicarbonate precipitates out and is separated and washed in a filtration step, after which it is converted to sodium carbonate by calcining at about 170 °C. The sodium carbonate formed, known as light ash, is purified and converted to dense ash form for sale. Alternately, sodium bicarbonate can be manufactured by further processing of the light ash.

[0010] The process described above recovers about 75-80 % of sodium carbonate and sodium bicarbonate into product, with the residual 20-25% remaining as a potential sodium chloride contaminant. The application envisages overcoming this by treating the brine with lime and hydrochloric acid, so as to produce relatively pure sodium chloride brine from which a salt can be recovered via evaporation and crystallisation. The application does not detail what waste streams would be produced during manufacture of the sodium chloride salt. The process is relatively complex, involving a large number of unit operations including the manufacture and recycling of concentrated carbon dioxide essential to the process. The limited recovery of sodium carbonate/bicarbonate salts results in a substantial hydrochloric acid demand in purifying the brine prior to sodium chloride manufacture. It also requires lime and a kiln to re-burn calcium carbonate, and a substantial evaporation/crystallisation plant to produce sodium chloride. Capital and operating costs for the process will be high relative to the modest value of the products produced.

[0011] A further problem with existing processes, in the context of the Queensland CSG industry, is that the salts recovered for beneficial use will likely be in excess of local demand, which will result in low or even negative returns for excess product sold into export markets (particularly for sodium chloride). The demand for soda ash and sodium bicarbonate in Queensland is about one third of potential production, and the products will be competing with imports, especially in SA, Victoria and NSW which are supplied by ANSAC/Penrice.

[0012] The aim of the present invention is to provide an economical process for manufacturing industrial grade sodium hydroxide and sodium chloride from brines, where the major dissolved salts are sodium chloride and sodium carbonate and/or sodium bicarbonate. The market for 46-50 % sodium hydroxide in Queensland is far in excess of potential production from waste brine, with about 1.4 million tpa consumed by the Gladstone alumina refineries, with most of this requirement imported. It will be appreciated that while the following description of the present invention makes frequent reference to CSG brines, this is primarily by way of example, and the present invention may be applied to manufacture sodium hydroxide and sodium chloride from any mixed brine stream whether occurring naturally (e.g. Sua Pan, Botswana) or arising as a waste.

[0013] The above discussion is included to put the invention in context, and is not to be taken as an admission that any of the material referred to was published, known, or part of the common general knowledge (in any country) as at the priority date of the claims.

SUMMARY

[0014] According to various embodiments, the present invention provides a cost effective method for processing brine where the major dissolved salts are sodium chloride, and sodium carbonate and/or sodium bicarbonate, such that industrial grade sodium hydroxide solution and sodium chloride salt are manufactured. The process transforms all water associated with the brine, which is not consumed by the process or products, into clean condensate. The invention overcomes shortcomings in the prior art by providing a less complex, lower cost processing method with zero liquid discharge, and which produces products suitable for industrial use without the need for substantial additional refining to purify the products.

[0015] The process of the present invention is particularly economical in terms of its use of reagents, requiring mainly lime which is for the most part recycled, and optional minor additions of chemicals to enhance product quality and/or process performance. The primary causticization stage of the process, in addition to converting sodium carbonate and sodium bicarbonate to sodium hydroxide, removes the main contaminants present in CSG brine, particularly magnesium and calcium hardness and a large proportion of the silica. This improves the purity of the products manufactured in the second stage of the process and significantly reduces scaling of process equipment.

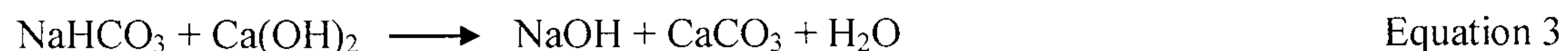
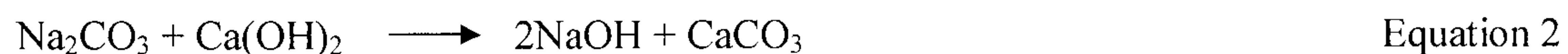
[0016] The second stage of the process takes advantage of the fact that sodium hydroxide has a high solubility relative to sodium chloride, for example at 60 °C 174 g of NaOH dissolves in 100 g of water, compared with just 34 g of NaCl. This enables the crystallisation of a relatively clean sodium chloride salt from the sodium hydroxide solution as the brine is concentrated in evaporator/crystallisers. A key advantage of the process is that due to the common ion effect, sodium chloride has a low solubility, less than 1.5% by mass, in sodium hydroxide solution at its ultimate concentration of 46-50 %. This enables recovery of more than 99 % of the sodium chloride present into industrial grade sodium chloride, and recovery of about 95 % of the sodium carbonate and sodium bicarbonate in the form of sodium hydroxide. The process of the present invention overcomes the problem of limited recoveries of both salts and water, and product contamination due to some co-precipitation of salts when concentrating/crystallising brines containing sodium chloride, sodium carbonate and/or sodium bicarbonate.

[0017] The process of the present invention is particularly well suited to processing brines containing a high concentration of sodium chloride and substantial levels of sodium bicarbonate and/or sodium carbonate. For example, the sodium chloride may comprise about 40-90 % by mass of the dissolved solids, and the sodium carbonate and/or sodium bicarbonate about 10-60 %. Contaminants such magnesium, calcium and silica can be accommodated by the process at their typical concentrations in CSG brine without unduly compromising product quality. On this basis Queensland CSG brines, which for example contain sodium chloride at about 60-80 % by mass of dissolved solids and sodium carbonate and/or sodium bicarbonate at about 20-40 % by mass of dissolved solids, are well suited to the process of the present invention. The process is applicable where the concentration of dissolved solids varies from about 1-6 %, as is the norm for saline effluent produced by the CSG reverse osmosis water treatment facilities, through to about 25 % dissolved solids (or the point of saturation) where the saline effluent has been further concentrated in evaporators to reduce it to a more manageable volume.

[0018] By way of example, the process of the present invention may be applied to reverse osmosis saline effluent which has been further concentrated by evaporation to about 16-22 % by mass total dissolved solids, which equates to 180,000-250,000 mg/l where the brine SG is about 1.14.

[0019] At this concentration the brine storage capacity requirements are greatly reduced, while brine concentration is kept below salt saturation levels which would complicate operation of the evaporators and brine storage and pumping systems. The composition of the brine, in terms of the mass % dissolved solids present, could for example be about as follows: 14.00 % NaCl, 3.12 % Na₂CO₃, 1.50 % NaHCO₃, 0.17 % MgCO₃, 0.07 % SiO₂ and 0.01 % CaCO₃ with about 81% water. Other salts such as potassium may be present, typically at levels of 0.2 % or less.

[0020] The process of the present invention may be applied to brine which has been pre-concentrated and stored for some time, or may preferably be integrated with the aforementioned evaporation stage so as to improve overall brine processing efficiency by utilising the heat present in the hot brine exiting the evaporator. If brine exiting the evaporators is used, it would likely be at about 80-100 °C, the preferred temperature to carry out the causticizing reactions, which convert the sodium carbonate and sodium bicarbonate components to sodium hydroxide through addition of lime. Quicklime (CaO) or hydrated lime (Ca(OH)₂) may be used, according to the following reactions:



[0021] In the process of the present invention the use of quicklime is preferred, such that the lime is mostly derived from calcium carbonate formed during the causticizing reaction, which is recovered and converted back to quicklime by burning in a lime kiln as established in the prior art. The hydration reaction of Equation 1 is strongly exothermic, providing some of the heat requirement to achieve and/or maintain a temperature of 80-100 °C during the causticizing process which is, in one of several possible configurations, conducted in a series of gravity flow continuously stirred tanks. Additional heating may be provided, for example through the use of steam, to achieve and maintain this temperature for the time required to obtain a conversion efficiency of 90 % or more, where the conversion efficiency (CE) of Na₂CO₃ and NaHCO₃ to NaOH during the causticizing process is defined as follows:

$$\% \text{ CE} = 100 \times \frac{(\% \text{ Na}_2\text{CO}_3 \text{ Eq. in Feed Brine} - \% \text{ Na}_2\text{CO}_3 \text{ Eq. in Exit Brine})}{(\% \text{ Na}_2\text{CO}_3 \text{ Eq. in Feed Brine})} \quad \text{Equation 4}$$

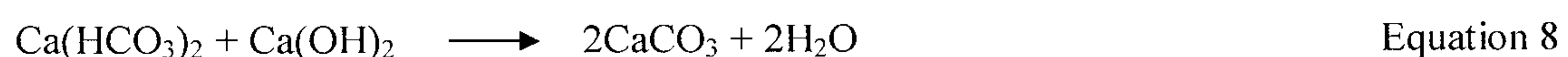
Where % Na₂CO₃ Eq. is a means of expressing the combined mass % of Na₂CO₃ and mass % of NaHCO₃ in the brine in terms of an equivalent (Eq.) mass % of Na₂CO₃:

$$\% \text{ Na}_2\text{CO}_3 \text{ Eq.} = \text{Mass \% Na}_2\text{CO}_3 + (0.631 \times \text{Mass \% NaHCO}_3) \quad \text{Equation 5}$$

[0022] Experimental work carried out in developing the process of the present invention has discovered that a surprisingly high conversion efficiency of about 97 % can be obtained when processing brine containing the major components described in [0019] despite a chloride concentration of about 5.3% (at 14.0 % NaCl). This finding is shown in Figure 1, which compares the conversion of Na₂CO₃/NaHCO₃ to NaOH when processing a brine containing 14.0 % NaCl, with the conversion obtained for liquor with the same alkali content but without any NaCl. At the relatively low alkalinity of about 4.1 % Na₂CO₃ Eq., the chloride has a negligible effect on the reaction, with about 90 % conversion achieved in 2 minutes, increasing to about 96 % in 10 minutes. The equilibrium conversion measured at 60 minutes is 97-98 %, both with 14.0 % NaCl and without any NaCl. This high conversion efficiency contrasts with experience from the Kraft process, where the conversion efficiency is typically in the 75-85 % range and is limited to less than 90 %. Furthermore, a low chloride concentration of 1.2 % in the Kraft process has been shown to further reduce conversion efficiency. The high conversion efficiency of the present invention is important in obtaining an efficient separation of brine components and to the quality of the products produced.

[0023] Experimental work carried out in developing the process of the present invention has discovered, as shown in Figure 2, that a lime dosage providing more than 110 % of the stoichiometric CaO requirement is required to achieve a high conversion efficiency of 96-98 %. A conversion efficiency of at least 95 % is preferred to minimise alkali impurities in the NaCl produced in the subsequent evaporation/crystallisation process and to maximise NaOH recovery. The experimental work indicated a satisfactory settling rate of the calcium carbonate at the 115-120 % lime dosage required to achieve 96-98 % conversion, and satisfactory filterability/dewatering properties of the resulting cake. This is significant in terms of experience from prior art in the paper/pulp industry where higher lime dosages have been observed to have a negative effect on settling and filtration.

[0024] The causticizing step of the present invention also serves an important purpose in removing some of the minor components present in the brine, which represent impurities in the process with respect to the sodium chloride salt and sodium hydroxide product, and which have the potential to cause severe operating difficulties in mechanical concentration and crystallisation of the brine. For example magnesium and calcium hardness are precipitated as magnesium hydroxide and calcium carbonate according to the following reactions:



[0025] Causticizing conditions are also conducive to the removal of silica, which at high pH is removed through the formation and precipitation of calcium-magnesium silicates, and through adsorption of silica on the magnesium hydroxide precipitate of Equation 7. Magnesium compounds (e.g. porous MgO) may be added to the brine to enhance silica removal by this mechanism. Iron and manganese are also largely removed during causticizing as they rapidly oxidise to insoluble form at high pH and are incorporated into the calcium and magnesium precipitates. Furthermore, reagents such as barium chloride can be added to the causticizing step to target the precipitation of specific impurities present in the brine (e.g. sulphates), and flocculants/coagulants can be added to enhance settling and filtration.

[0026] The effectiveness of the causticizing step of the present invention in removing calcium, magnesium, silica and other contaminants has been proven through an experiment which compared contaminant levels in concentrated Queensland CSG reverse osmosis brine with the same brine after subjecting it to causticizing. The CSG reverse osmosis brine used in the experiment was concentrated by evaporation from a TDS of about 10,300 to 70,000 mg/l. The concentrated brine was heated to 90 °C and slaked lime was added at a dosage in excess of 110 % of the stoichiometric CaO requirement. After stirring continuously for 60 minutes the causticized brine slurry was filtered to separate out unreacted lime, CaCO₃ and precipitated contaminants, producing a clear causticized brine at a conversion efficiency of 98 %. Samples of the concentrated untreated brine and causticized brine were submitted to a NATA accredited laboratory for analysis, providing the results presented in Table 1 below:

TABLE 1

Comparison of Contaminant Levels in Untreated and Causticized Brine

Brine Contaminant	Untreated Brine	Causticized Brine
Calcium as Ca (mg/l)	34	19
Magnesium (mg/l)	9.8	<5
Silica as SiO ₂ (mg/l)	270	44
Barium as Ba (mg/l)	9.0	0.5
Strontium as Sr (mg/l)	11.0	0.3
Iron as Fe (mg/l)	0.15	<0.02
Fluoride (mg/l)	126	87
Potassium as K (mg/l)	140	130

[0027] The results in Table 1 show that more than 40 % of the Ca and Mg contaminants in the brine were removed by the causticizing process. This is significant in terms of the suitability of the brine for production of industrial grade NaCl salt. The Ca level in untreated brine equates to a Ca contaminant level of up to 870 ppm in produced salt, whereas the reduced Ca level in causticized brine equates to a Ca contamination level of less than 500 ppm, which is the upper Ca limit used by major producers of industrial grade salt like Dampier. The Mg level in causticized brine is also considerably reduced, and would result in a contamination level in salt less than half of the 300 ppm upper limit imposed by Dampier.

[0028] The large reduction in silica, which can be over 80 % based on the experimental data, combined with the reduction in calcium and magnesium is significant from the point of view of reducing scale deposits in mechanical evaporation and crystallisation processes used in concentrating brine and/or producing products. Scaling of heat transfer surfaces occurs through a variety of mechanisms, including co-precipitation of silica with calcium and magnesium compounds, hence a reduction in the concentration of all three elements greatly reduces the potential for scale formation. Furthermore, the solubility of silica increases with pH, hence silica will have a greater tendency to remain in solution during concentration and crystallisation of causticized brine as compared to uncausticized CSG brine.

[0029] In the process of the present invention the precipitates of the impurities are separated from the causticized brine during the settling/thickening and filtering of the calcium carbonate formed during the causticizing reactions of Equations 2 & 3. The primary liquid/solid separation is carried out in a settling tank which produces a clear causticized brine overflow, and thickened calcium carbonate slurry, typically containing about 25-40 % solids. This slurry is filtered, and the resulting filter cake is washed with hot condensate recovered in the second stage of the process and dewatered to increase the solids content to about 45-75 %. The use of recycled hot condensate improves the efficiency of the washing process in removing entrained brine from the filter cake, and assists in reducing moisture content of the cake. The calcium carbonate, containing minor levels of removed impurities, is burnt in a kiln so as to recycle it back to quicklime. Excessive build-up of impurities is prevented if necessary by bleeding off some of the calcium carbonate cake, or some of the lime which can potentially be sold.

[0030] The causticized brine overflow from the settling tank and filtrate from the calcium carbonate filter are combined into a single stream. This stream may, depending upon the required quality of sodium chloride salt and sodium hydroxide, be further treated to remove any residual particulates and further reduce brine impurities. For example, the brine may be passed through additional filters, including membrane ultra-filtration, or may be treated using electrocoagulation.

[0031] The brine, containing the original sodium chloride dissolved salts and sodium hydroxide, as well as a small proportion of unreacted sodium carbonate, is routed through an evaporator/crystalliser plant. The causticized brine composition when derived from the CSG brine described in [0019], and based on a conversion of 95 %, is for example about as follows: 13.80 % NaCl, 2.87 % NaOH and 0.19 % Na₂CO₃. Slight dilution of the brine occurs due to incorporation of the condensate used in filter cake washing. The purpose of the evaporator/crystalliser plant is to increase the sodium hydroxide concentration to a 46-50 % industrial strength product, while separating out and washing the sodium chloride crystals as they precipitate out of solution in accordance with their low solubility in concentrated caustic.

[0032] The evaporation/crystallisation process can be conducted in equipment of various designs, including multiple effect evaporator/crystallisers, or in mechanical vapour recompression evaporators which feed a crystalliser circuit. Separation and washing of sodium chloride crystals is generally best carried out using centrifuges, assisted if necessary by hydro-cyclones. In the process of the current invention a small portion of the hot condensate recovered from the evaporators is used to rinse caustic solution from the salt crystals, with the wash solution returned to the evaporator/crystallisers ensuring maximum recovery of sodium hydroxide, and reducing sodium hydroxide contamination of salt.

[0033] The solubility of sodium chloride in 46-50 % sodium hydroxide is low, hence once the caustic product has reached this strength about 99 % of the sodium chloride present in the causticized brine described in [0031] has crystallised out, leaving only a small amount of sodium chloride in the caustic, which equates to a contamination level of about 0.9-1.5 %. This is consistent with the typical quality of industrial grade diaphragm cell caustic, and is suitable for many uses, including the Bayer process used in alumina refining.

[0034] If required the sodium chloride level in the caustic may be reduced by a number of methods, well known to those familiar with the art of purifying diaphragm cell caustic.

[0035] The solubility of sodium carbonate in 46-50 % caustic is also low, at about 1-4 g/kg caustic solution, depending on the temperature. Hence most of the unconverted sodium carbonate will co-precipitate with the salt, typically resulting in about 0.1-0.2 % sodium carbonate in the caustic product following cooling to about 40 °C. Hence, in the process of the present invention the 46-50 % caustic leaving the evaporator/crystallisers is cooled to 40 °C or less, and then relieved of any super-saturation in a stirred crystalliser vessel before being passed through a filter or other suitable solids/liquid separation process to remove crystals of salt and/or sodium carbonate formed on cooling. Cooling to a lower temperature, for example about 15-20 °C, can be used to reduce the level of impurities in caustic if required.

[0036] In the process of the present invention the small quantity of crystals formed following cooling are added to the salt, or are recycled to the first vessel of the causticizing process, depending upon their quality and quantity. For the causticized brine described in [0031], the sodium carbonate present will represent a maximum of about 0.8 % of the sodium chloride mass. Higher sodium chloride purity can be obtained by improving the causticizing efficiency, by washing the salt, or by adding hydrochloric acid to the salt to convert the sodium carbonate to sodium chloride. The present invention incorporates a process design for washing of the salt in a circulating saturated NaCl liquor which is dosed with hydrochloric acid at a rate just sufficient to convert entrained NaOH and unconverted sodium carbonate into NaCl, ensuring a high purity of the salt with respect to alkalinity if this is required.

[0037] In an alternative embodiment of the present invention, the causticizing step is carried out on the saline effluent generated by CSG reverse osmosis plants, typically with TDS in the 10,000 to 60,000 mg/l range, prior to concentration by evaporation, or after some limited concentration by evaporation aimed at avoiding scale deposition in the evaporators. Experiments were conducted on low salinity RO effluent from a Queensland CSG water treatment plant with a TDS of about 10,300 mg/l. The experiments confirmed the effectiveness of the causticizing step on the RO plant effluent with about 97 % conversion achieved after 5 minutes at a lime dosage of 120 % of the stoichiometric CaO requirement and at a temperature of 90 °C. In this embodiment subsequent process steps are as described from [0024] onward, except that the evaporation process described in [0031] and [0032] involves driving off a lot more water before the causticized brine reaches NaCl saturation. This embodiment may be of particular benefit where the RO plant effluent contains problematic levels of Ca, Mg, Si or other contaminants which would result in severe scale deposition when concentrating uncausticized brine in mechanical evaporators.

DESCRIPTION OF DRAWINGS

[0038] Figures 1 & 2 show the results of laboratory experiments conducted to determine and optimise the conversion efficiency for the first stage of the process of the current invention. Figure 3 shows a process flow diagram according to the preferred embodiment of the present invention. It is to be appreciated that the following description only exemplifies one way of putting the present invention into practice. The following description is thus not to be read as limiting the above general description.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0039] Referring to Figure 3: Brine **1**, containing at least sodium chloride, and sodium carbonate and/or sodium bicarbonate as major components is heated and transferred into a series of continuously stirred tanks **2**, configured for gravity flow from the first to the last tank. Heating is controlled, depending on whether the brine is received hot from upstream brine concentrators and on whether quicklime or hydrated lime is utilised in the process, so as to achieve a tank operating temperature of about 85-100 °C. Quicklime **6** is fed into the first tank via lime storage silo **4** and lime dosing system **5**. Alternately, quicklime from the dosing system can be slaked and de-gritted in a hydrator prior to addition to the first tank. Lime is added at an excess to the theoretical requirement, preferably at 110-130 % of the calculated stoichiometric CaO requirement for the causticizing reaction. A conversion efficiency of 95 % or more is achieved in a series of 2-5 tanks, with residence time of 0.5-2 hours.

[0040] Upon leaving the last tank the causticized slurry **8** is pumped via centrifugal pump **7** to a settling tank/thickener **9** where the calcium carbonate settles readily, forming slurry containing about 25-40 % solids. The thickened slurry **12** is pumped via underflow pump **10** to filter **14**, which separates the slurry into causticized brine filtrate **15** and filter cake **16** containing about 45-75 % solids. The preferred filter design allows efficient washing of the calcium carbonate cake with recycled hot condensate **13** so as to maximise removal of entrained brine, while minimising moisture content of the cake prior to the kiln. To control build-up of impurities in the lime circuit, for example magnesium, calcium and silica precipitated out of the brine, a small amount of filter cake is removed in a bleed stream **19**, or alternately the bleed may be taken as quicklime **23** if the lime can be sold into local markets. The calcium carbonate **21** is fed to a kiln **22** through a storage/metering system **20** where it is converted back into quicklime **23** for use in the causticizing process. Make-up lime **3** is added to compensate for losses through the process and for bleed stream **19**.

[0041] The causticized brine overflow **11** from the settling tank/thickener **9** is combined with the brine filtrate **15** and may, depending on the required quality of sodium hydroxide and sodium chloride salt, be subjected to further treatment/filtration **17**. The small quantity of impurities/salts removed **18** are combined with the purge stream **19** for disposal, while the clarified/purified brine is routed to a brine storage tank **24** which feeds the evaporator/crystalliser stage of the process.

[0042] In the preferred embodiment, the evaporator/crystalliser plant is, for reasons of energy efficiency, comprised of multiple effect evaporators (preferably 3-4 effects) or one or more mechanical vapour recompression (MVR) evaporator equipped with a separate crystalliser operating on a concentrated brine side stream from the MVR evaporator. The design may incorporate preheating 26 of the feed brine 27 delivered to the evaporator/crystalliser 28 by the feed pump 25, though this is not required where multiple effect evaporators operating under a vacuum are used with brine from the causticizing stage at 70-80 °C. For the sake of simplicity the evaporator/crystalliser stage is represented as a single unit in Figure 3, though in practice there will frequently be multiple units configured either in series or parallel.

[0043] Where multiple effect evaporators are used, the evaporator receiving the brine, which is well below saturation in sodium chloride following causticizing, may be of a compact efficient configuration such as falling film design, since crystallisation of sodium chloride on the heating surface will not occur until the solution approaches saturation. The preferred configuration for subsequent evaporator/crystallisers receiving near saturated or saturated brine are of forced circulation design with a circulating pump 30 and an external heat exchanger 31, such that boiling and concentration of the brine is prevented at the heat exchange surface, occurring as the superheated brine is returned into the evaporator/crystalliser body 28. The evaporator/crystalliser body incorporates an elutriating leg 32, whereby brine containing sodium chloride crystals of adequate size is extracted and passed through a centrifuge 33 or hydro-cyclone and centrifuge to separate crystallised salt from the brine as the sodium hydroxide concentration increases, and sodium chloride solubility decreases. A small amount of hot condensate 35 is used to wash sodium hydroxide off the salt and return it to the evaporator/crystalliser, while the sodium chloride product 36 is discharged, either to a product stockpile 37, or to a salt washing/alkali neutralisation stage, depending on the acceptable level of alkali impurities in the NaCl product.

[0044] The salt washing process operates with a circulating saturated NaCl liquor so as to avoid dissolution of the salt crystals. The salt is fed to a stirred wash tank 38, where neutralisation of entrained NaOH and unconverted sodium carbonate is achieved through addition of hydrochloric acid 43 which converts the alkalis to NaCl. The small amount of NaCl formed precipitates out as fine salt crystals, which are separated from the circulating liquor by means of a centrifuge 40 together with the washed salt. The treated salt 41 is routed to the product stockpile 37 and wash liquor 42 is returned to the wash tank.

[0045] In a preferred three effect evaporator embodiment of the current invention, the evaporator/crystalliser producing 46-50 % caustic solution operates under pressure, for example at 250 kPa absolute so that the caustic liquor temperature is about 163 °C and water vapour driven off is at 126 °C, suitable for heating the adjacent unit. A suitable operating pressure for the adjacent unit is 101 kPa absolute, so that the brine liquor temperature is about 108 °C and the water vapour driven off is at 100 °C, suitable for heating the adjacent unit. This unit operates under negative pressure, for example 40 kPa absolute, such that the brine liquor temperature is about 82 °C and water vapour temperature is 76 °C. The heat source for the process is steam at about 180 °C and 1,000 kPa absolute, provided to the evaporator/crystalliser which operates at about 163 °C. Steam is required at a rate of about 1.0 tonne of steam per 2.4 tonne water evaporated. The water vapour 44 from the evaporators is cooled, either by providing heat to the adjacent unit through a heat exchanger 31 or by cooling water 45 for the low temperature unit. The resulting condensate 46 from all of the evaporators is combined into a storage tank 47, with some of it recycled for washing of the calcium carbonate filter cake 13, and some of it used for washing of sodium chloride salt 35. The water quality of the condensate is such that it is suitable for a range of other uses.

[0046] In an alternative embodiment, the evaporator/crystalliser is of MVR design. In this case the design may incorporate single or multiple MVR units. In a preferred embodiment of the current invention utilising the MVR principle, the design incorporates two units, with the first being an evaporator of falling film design which concentrates the causticized brine solution to just below the level of sodium chloride saturation. The second unit, which concentrates the brine to a caustic liquor concentration of 46-50 %, incorporates forced circulation through a heat exchanger and a centrifuge to separate out and wash sodium chloride crystals. It will be appreciated by those skilled in the art of evaporation and crystallisation that the embodiments described represent just two ways of concentrating the causticized brine to about 46-50 % sodium hydroxide, while recovering sodium chloride salt of satisfactory purity for industrial use. Various other evaporator/crystalliser configurations can be used within the scope of the present invention.

[0047] The sodium hydroxide solution **48**, which leaves the evaporator/crystallisers at about 163 °C, is cooled in a heat exchanger **49** to about 15-40 °C before being routed to a continuously stirred tank **51**, where super-saturation of sodium chloride and sodium carbonate is relieved. Since the solubility of sodium carbonate and sodium chloride reduce with decreasing temperature of the sodium hydroxide, the product purity can to an extent be improved through additional cooling to about 15-20 °C, especially with respect to sodium carbonate. Cooling the solution to 40 °C results in a sodium hydroxide solution with about 1.0-1.3 % sodium chloride, and sodium carbonate of less than 0.2 %, consistent with the purity of industrial grade diaphragm cell sodium hydroxide. Cooling to 15-20 °C reduces the sodium carbonate impurity to about 0.1 %, while also reducing the sodium chloride impurity to 1.1 % or less.

[0048] Other methods of reducing the level of impurities, well known to those familiar with the art of diaphragm cell sodium hydroxide manufacture, may be used to improve the purity of the product if required. For example the sodium hydroxide may be further concentrated, to well above 50 %, forcing precipitation of additional sodium chloride and sodium carbonate crystals, after which it may be diluted with clean condensate back to a 46-50 % solution. Alternately the sodium hydroxide solution may be contacted in a column with an ammonia solution, which absorbs the sodium chloride.

[0049] After relief of super-saturation, the sodium hydroxide solution leaving the stirred tank **51** is passed through a filter **52** to separate out the sodium chloride/sodium carbonate crystals **54**, which are either routed to the salt washing/neutralisation process **38**, or are recycled back to the causticizing process **2**. The sodium hydroxide **53** is stored in a product tank **55** ready for shipment to customers.

CLAIMS

What is claimed is:

1. A process for manufacture of sodium hydroxide and sodium chloride products from a brine stream containing at least sodium chloride, and sodium carbonate or sodium bicarbonate (or a mixture of sodium carbonate and sodium bicarbonate), which comprises at least the following steps:
 - a) converting the sodium carbonate and sodium bicarbonate present to sodium hydroxide through addition of lime to the sodium chloride rich brine;
 - b) separating the causticized brine from unreacted lime and calcium carbonate formed;
 - c) concentrating the causticized brine via evaporation of water such that sodium chloride crystals form;
 - d) separating the sodium chloride crystals from the saturated solution;
 - e) continuing the evaporation/crystallisation process until only a concentrated sodium hydroxide solution remains.
2. A process according to claim 1, which includes the additional steps of:
 - f) recycling all or most of the unreacted lime and calcium carbonate recovered at (b) for reuse in (a) by burning in a kiln to convert calcium carbonate back to calcium oxide;
 - g) reducing unwanted impurities in the brine through their co-precipitation during (a), without or with addition of mineral/chemical reagents, and separation of precipitated impurities together with the unreacted lime and calcium carbonate at (b);
 - h) bleeding off a portion of the unreacted lime, calcium carbonate and impurities of (g), or a portion of the burnt lime of (f), as required to control the build-up of impurities in the lime cycle of (f).
3. A process according to claim 2, which includes the additional steps of:
 - i) cooling the concentrated sodium hydroxide from (e) and crystallising out and separating a portion of the remaining sodium chloride and sodium carbonate impurities so as to produce an industrial grade sodium hydroxide product;
 - j) combining the crystallised sodium chloride and sodium carbonate from (i) with the sodium chloride crystals from (d), either directly or following treatment with hydrochloric acid; or recycling the crystallised sodium chloride and sodium carbonate from (i) back to sodium chloride rich brine at (a).

4. A process according to claim 3, which includes the additional steps of:
 - k) washing the sodium chloride crystals from (d) with a small amount of clean water recovered from evaporation at (c) and (e) so as to displace residual sodium hydroxide from the surface of the salt crystals, hence minimising sodium hydroxide contamination, with the washings returned to the evaporator/crystallisers so as to maximise sodium hydroxide recovery;
 - l) optionally, washing the salt crystals recovered from (d) and/or (i) in a sodium chloride saturated brine solution dosed with hydrochloric acid so as to convert the residual alkalis (mostly Na_2CO_3) to sodium chloride, followed by separating out the purified salt crystals from the saturated brine solution which is recirculated back to the washing/acid treatment process.
5. A process according to claim 4, which includes the additional step of:
 - m) purification of the causticized brine from (b), for example by membrane ultra-filtration or electro-coagulation to remove unwanted impurities, prior to evaporation/crystallisation at (c)
6. A process according to claim 2, which includes the additional steps (k) and/or (l).
7. A process according to claim 2, which includes the additional step (m).
8. A process according to claim 6, which includes the additional step (m).
9. A process according to claim 3, which includes the additional step (m).
10. A process according to claim 1, which includes the additional steps (i) and (j).
11. A process according to claim 10, which includes the additional steps (k) and/or (l).
12. A process according to claim 10, which includes the additional step (m).
13. A process according to claim 11, which includes the additional step (m).
14. A process according to claims 1, 2, 3, 4 and 5 wherein the conversion of sodium carbonate and sodium bicarbonate to sodium hydroxide is carried out in the presence of an unusually high concentration of chloride ions relative to causticizing reactions in the pulp (Kraft) and alumina refining (Bayer) processes, for example four times higher than in pulp mills operating with relatively high chloride levels.
15. A process according to claim 14 where optimising the lime dosage in the causticizing step at above 110 % of the stoichiometric CaO requirement enables attainment of an unusually high conversion efficiency of at least 90 %, and preferably 95-99 %, such that sodium carbonate contamination of the sodium chloride and sodium hydroxide products is minimised.

16. A process according to claim **15** where causticizing of the brine and subsequent separation of precipitated calcium carbonate/unreacted lime enables calcium, magnesium and silica contaminant levels in brine to be reduced by more than 40%, enabling industrial grade NaCl and NaOH to be produced without additional refining steps, and significantly reducing the potential for scale deposition in the evaporation/crystalliser equipment.

17. A process according to claim **16** where the sodium hydroxide produced is suitable for a range of industrial applications, being of comparable quality to that produced by the diaphragm cell process, having a preferred NaOH concentration of 45-51 % by mass, and containing less than 1.5 % NaCl and 0.3 % Na₂CO₃ contaminants by mass.

18. A process according to claim **17**, where the sodium chloride produced is of suitable quality for a range of applications, including the chlor-alkali industry, containing less than 500 ppm Ca and 300 ppm Mg, and less than 0.8 % sodium carbonate, which can optionally be reduced through the hydrochloric acid wash process (I).

19. A process according to claim **18** where the primary evaporation step to bring the causticized brine close to saturation in sodium chloride is carried out in evaporators which provide a high rate of heat transfer and high energy efficiency (e.g. falling film multiple effect or falling film MVR evaporators) and where the secondary evaporation/crystallisation of saturated brine occurs in forced circulation evaporators capable of growing sodium chloride crystals suitably sized for efficient separation and washing, while preventing salt build-up on heat exchange surfaces.

20. A process according to claim **19** where the brine stream processed is a waste derived from the treatment of water co-produced during coal seam gas extraction.

DRAWINGS

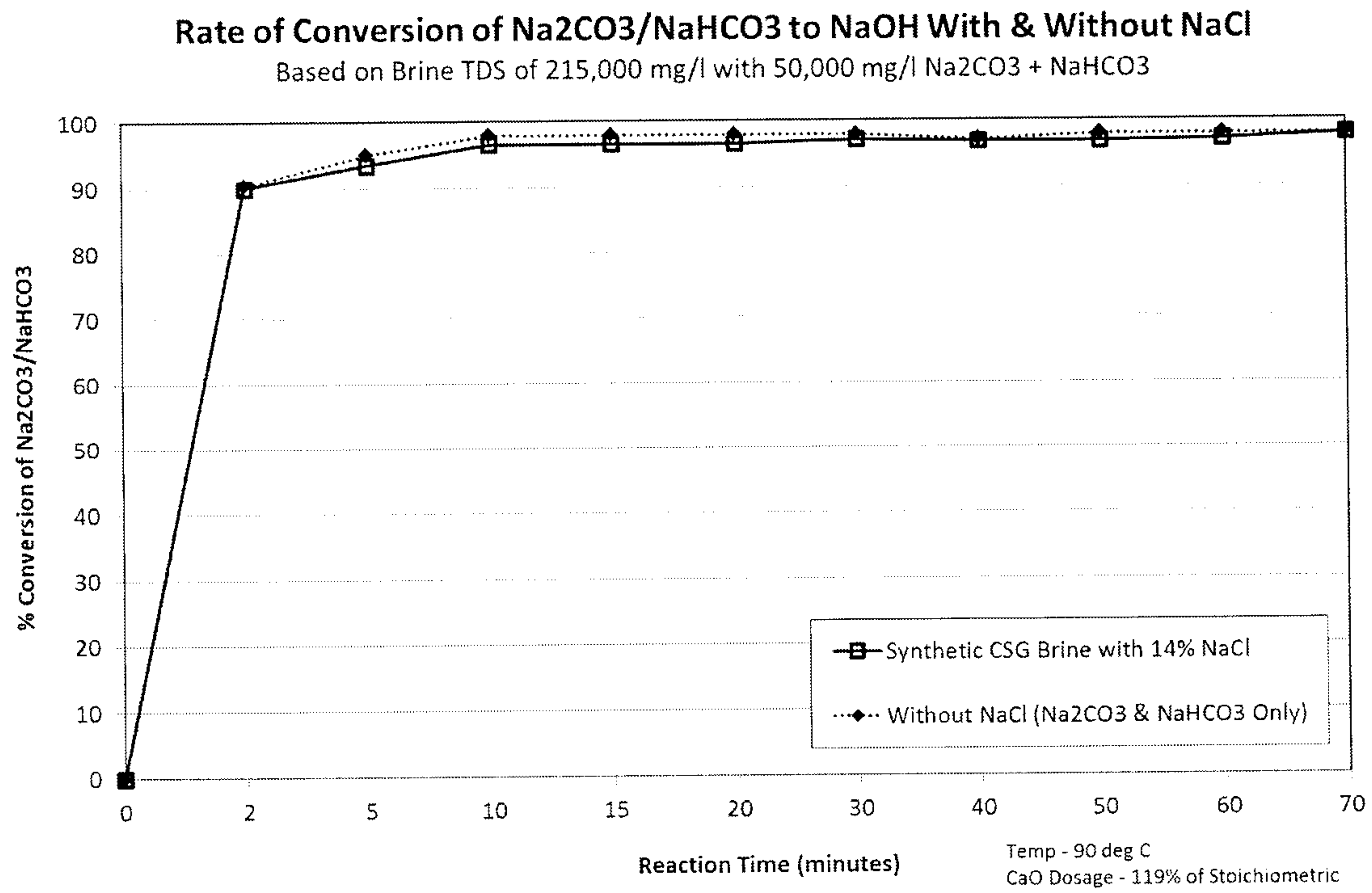


Figure 1

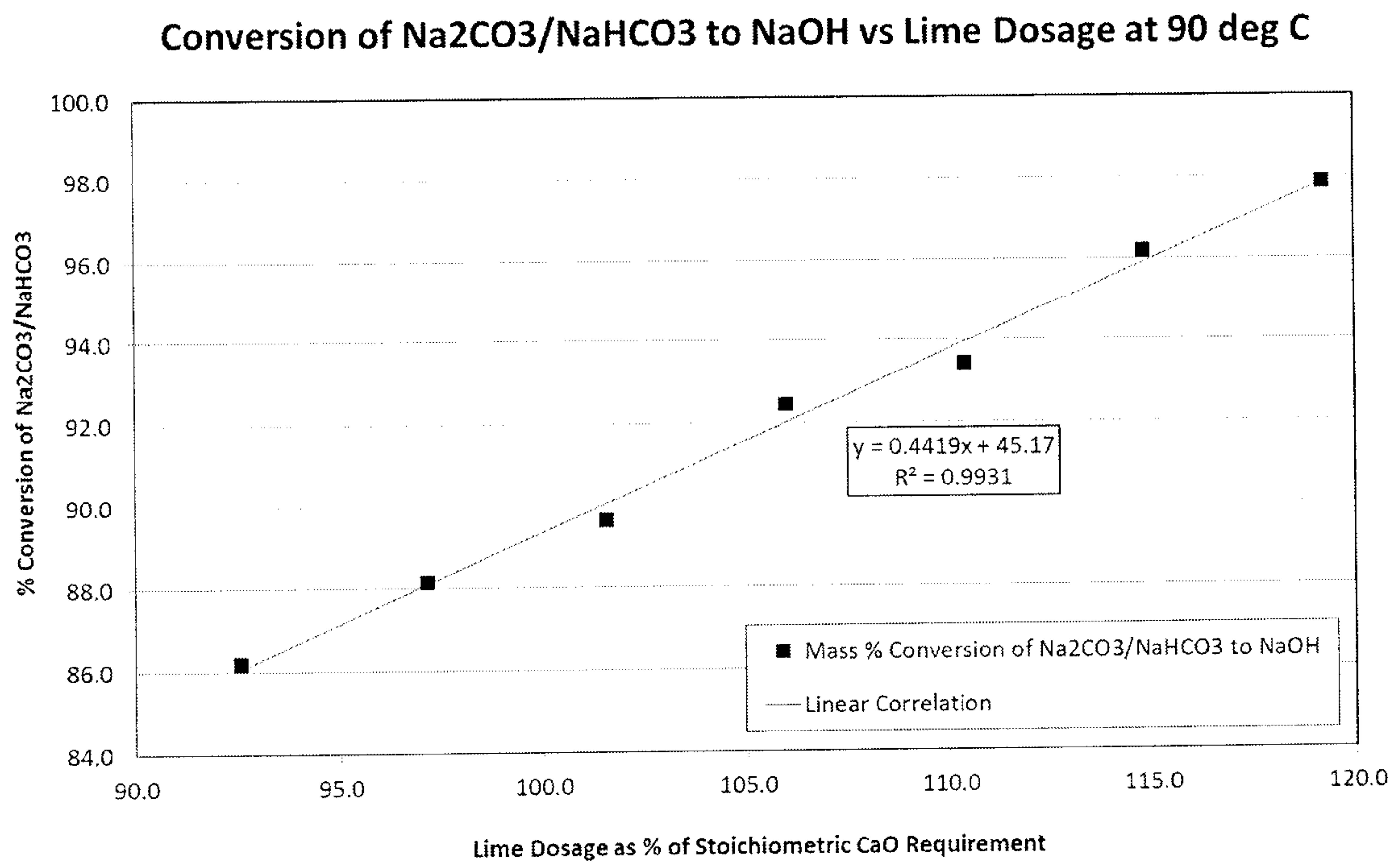


Figure 2

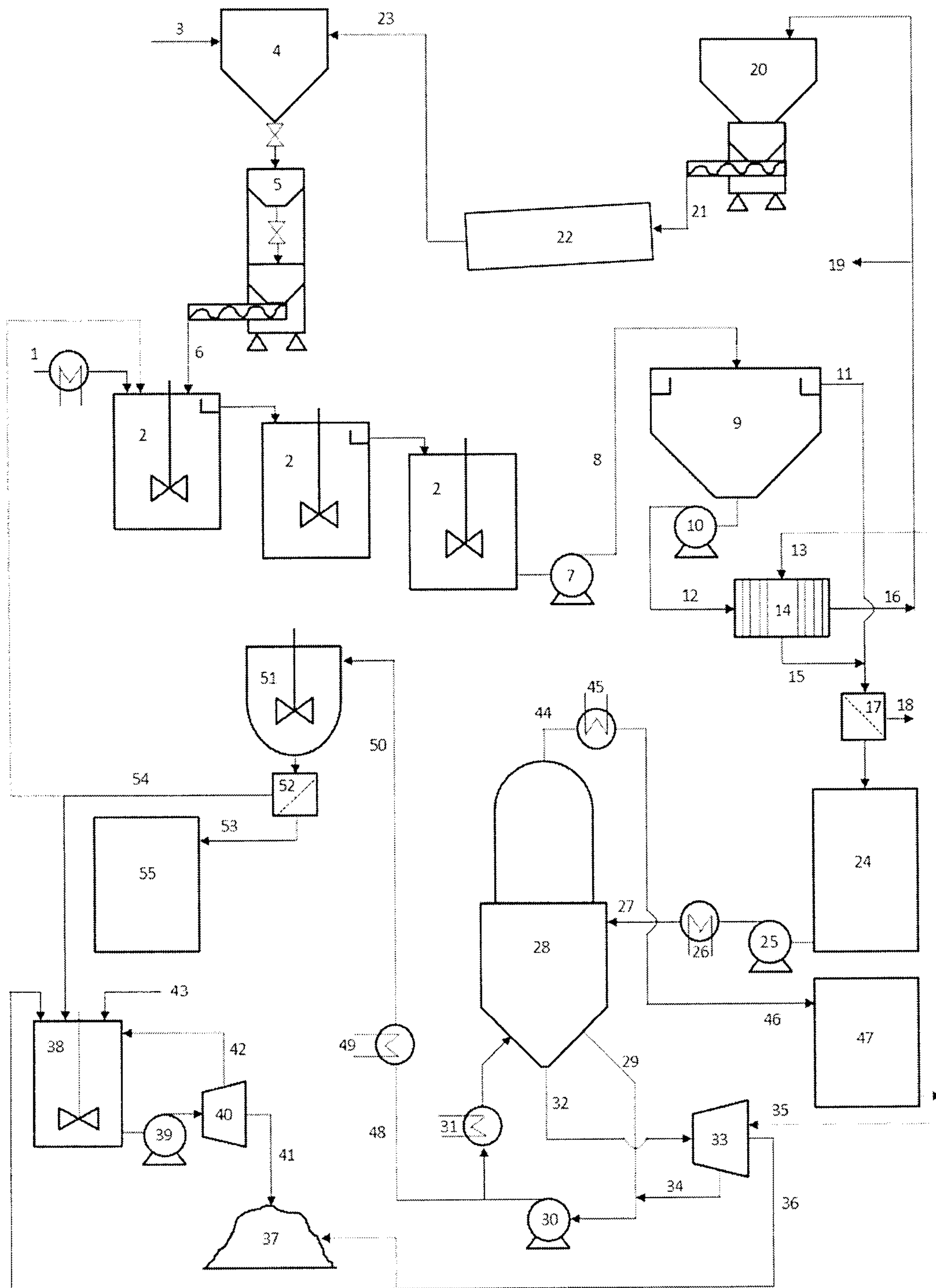


Figure 3

